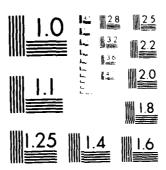
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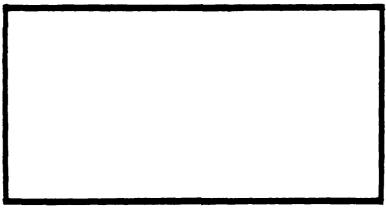


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Dennis C. Hughes, Captain, USAF

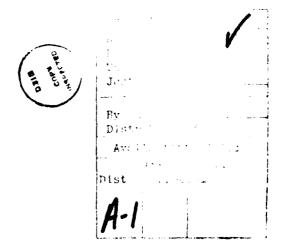
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Water samples taken from a high-pressure, high-horsepower steam boiler system were used to investigate the need and feasibility of incorporating current preservation/ stabilization techniques into the Air Force industrial water analysis program and to study the effect that a time delay between sample collection and analysis of the sample by an independent lab has on the analysis results. The boiler water constituents studied were phosphate, sulfite, and causticity in the daily samples taken from the on-line boiler system. Samples were placed into either a control group, a preserved/stabilized group, or an unpreserved group depending upon the treatments the samples received. The analysis of the constituents were conducted in accordance with the procedures prescribed in AFM 85-12, Volume 1. Results indicate that the current preservation/stabilization techniques were not effective in preventing changes in the concentrations of the constituents studied. The effect that time has on the boiler water constituents is an important aspect which must be considered when reviewing the results of the independent analysis with respect to the recommendations outlined in AFM 85-12, Volume 1.

INDUSTRIAL WATER ANALYSIS PROGRAM: A CRITICAL STUDY

A Thesis

Presented to the Faculty of the School of Systems and Logistics of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Engineering Management

Ву

Dennis C. Hughes, BS Captain, USAF

September 1983

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This thesis, written by

Captain Dennis C. Hughes

has been accepted by the undersigned on behalf of the faculty of the School of Systems and Logistics in partial fulfillment of the requirments for the degree of

MASTER OF SCIENCE IN ENGINEERING MANAGEMENT

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Paul A. Richard, Lt Col, PhD Committee Chairman

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CHAPTER I

INTRODUCTION

Chapter Overview

This chapter contains a general background on the industrial water analysis procedures in the United States Air Force and the problems experienced in making the procedures effective. The specific problem investigated in this study is stated, and the research objectives and research questions are listed. Also in this chapter are the scope and limitations of the study, research assumptions, definitions of terms frequently used in the research, a description of the current Air Force industrial water analysis program, and the description of the national standards and how they relate to this research effort.

The Air Force Industrial Water Analysis Program

Air Force installations depend on either steam or hot water boiler systems to supply their varied heating requirements. The Air Force has approximately 700 steam boiler systems in service throughout its installations worldwide to provide this vital requirement. The water used in these boiler systems needs to be monitored on a

continuous basis in order to protect the substantial investment made in the equipment. An uncontrolled situation could allow pitting of the metal surfaces, which could cause system leakage or possibly lead to the destruction of the boiler itself. The monitoring program also serves the vital function of helping to stabilize the systems' efficiency.

The monitoring program is carried out through systematic sample collection and testing of the industrial water used in the boiler systems. Industrial water samples have to be taken at varying times specified in AFM 85-12, Boiler Water Treatment Volume 1, with frequency ranging from daily to weekly, depending on boiler type. Schedules by type are presented later in this study.

Air Force personnel at installations where boiler systems are used collect the samples and immediately analyze the quantity of the constituents contained in the boiler water sample. The testing procedures used by the Air Force personnel are outlined in AFM 85-12, Volume 1. These testing procedures are presented as part of the methodology contained in Chapter II.

As a quality control check on the Air Force industrial water analysis program, an extra identical sample is shipped to an independent laboratory for analysis. The submission schedule for these check samples varies from

monthly to quarterly depending on boiler type. The schedule is described in detail later in this chapter.

Currently, the independent analysis program, which is provided through an interim contract, handles only 624 samples per year on a worldwide basis; however, it is estimated that the program will handle approximately 4000 samples worldwide on a yearly basis when the full capacity of the program is realized. The \$35.00 per sample fee currently charged for this quality control precaution could cost the Air Force \$140,000.00 each year.

Problem Statement

The results of the independent laboratory analysis are used as a comparison with the results obtained from the daily on-site analysis. Although the samples are drawn at the same time and should be identical, differences exist between the Air Force results and the results reported by the independent laboratory. As an example of these differences, the results of the samples drawn on 6 December 1982, from boiler #5, Building 770, at Wright-Patterson Air Force Base, Ohio, differed by 96 percent on the quantity of reported sulfite, by 94.2 percent on the quantity of reported phosphate, and by 40.43 percent on the value for causticity. These differences were not just a one-time occurrence, as the list in Appendix A illustrates.

It is essential that the reasons for these differences be discovered. The resultant damage that could
occur due to the improper chemical composition of the
boiler water can have an adverse affect on the efficiency
of the boiler system or, in fact, may result in the loss
of the substantial investment the Air Force has in these
boiler systems.

AFM 85-12, Volume 1, asserts that the independent laboratory's results should be the more accurate. However, this may not be the case. According to Standard Methods and 1982 Annual Book of ASTM Standards, Part 31, the results obtained from immediate field testing are more accurate for certain constituents and physical values. The independent laboratory analyzes the samples from Wright-Patterson Air Force Base approximately 14 days after they are drawn. In addition, the samples they receive and test have not been chemically stabilized or preserved before shipment to the laboratory. A possible cause for the differences in the analysis result is:

changes in sample constituency and make-up caused by chemical, physical, or biological reactions occurring between the time the sample is collected and the time the sample is analyzed by an independent laboratory [2:44].

Research Objectives

The objectives of this study are the following:

1. Review the current Air Force practice of sending non-preserved/non-stabilized samples to the independent laboratory in light of current, accepted scientific practices to determine if the differences between the scientific practices and the Air Force procedures are contributing to the differences between the Air Force test results and the independent laboratory test results.

2. Conduct an experiment to demonstrate the effect of sample preservation/stabilization procedures on the test results.

Research Questions

The questions to be answered in this study are the following:

- What effects, if any, on analysis results are caused by the current lack of sample preservation/ stabilization?
- 2. If the lack of preservation/stabilization techniques contributes to the differences in the analysis results, what techniques would eliminate the situation?

Assumptions

- National standards, which reflect current,
 standard scientific practices, are appropriate guides.
- Proper sample collection techniques are being used.
- Proper laboratory test analysis procedures are being used by all concerned.

Scope and Limitations

The scope of this study is limited to investigating the areas of testing highlighted by either the 14th edition of Standard Methods or 1982 Annual Book of ASTM Standards,

Part 31 as having an appropriate existing preservation/
stabilization procedure that could be applicable. The constituents that will be examined in the boiler water are of phosphate, hydroxide, and sulfite. The experiment that will be used in this study will be limited to the high pressure boiler systems housed in Building 770 at Wright-Patterson Air Force Base, Ohio. The details of this experiment will be explained in the methodology section of this study.

Definition of Terms

The following terms, used frequently throughout this study, are defined as follows:

- Alkalinity: the quantitative capacity of aqueous media to react with hydrogen ions [11:p.Al-1].
- Amines: a group of volatile, alkaline compounds that neutralize the carbonic acid in the return lines [10:287].
- Blowdown: the process of draining a portion of water from a system to reduce the concentration of dissolved solids, or to discharge accumulations of material carried by the water, as used in connection with boilers [ll:p.Al-l].
- Cation: a positively charged ion of an electrolyte, which migrates toward the cathode under the influence of a potential gradient [ll:p.Al-l].
- Caustic Soda: [a sodium hydroxide solution which] provides alkalinity [causticity] in the form of free hydroxide [10:258].

- Causticity: amount of free alkali or hydroxyl ions liberated when alkaline salts or caustics are dissolved in water [ll:p.Al-l].
- Condensate: condensed steam which has been cooled in the plant heating or process system and returned to the boiler system [7:2].
- Corrosion: destruction of a metal by chemical or electrochemical reaction with its environment [11:p.Al-2].
- Dissolved Solids: the material, usually minerals, dissolved in water; the dried residue from evaporation of the filtrate after separation of suspended solids [suspended matter] [ll:p.Al-2].
- Feedwater: water being applied to the feedwater heater or to the boiler in a power plant and consists of both makeup and condensate [7:2].
- Hardness: a characteristic of water that represents the total concentration of just calcium and magnesium ions expressed as calcium carbonate [2:200].
- Industrial Water: refers to the water used in Air Force power, heating, air conditioning, refrigeration, cooling, processing, and all other mechanical and electronic equipment and systems that require water in their operation [ll:p.l-l].
- Makeup Water: water supplied to replenish that lost in a system by leaks, evaporation, bleedoff, blowdown, withdrawal, etc. [ll:p.Al-2].
- Preservative: Any agent that retards or prevents the decay discoloration, or spoilage of a substance under the conditions of storage or nonchemical use [2:pp.43-44].
- Scale: a deposit formed from solution directly upon a surface [3:3].
- Sludge: a water-formed sedimentary deposit which may include all suspended solids carried by water . . . [11:p.Al-3].
- Sodium metaphosphate: phosphate chemical added to boiler water to combine with calcium to precipitate calcium phosphate and . . . readily removed by blowdown . . . Phosphate control prevents formation of calcium scales . . . [10:258].

- Sodium sulfite: sulfite chemical added to boiler water to remove the last traces of oxygen to improve corrosion control of the system [10:286].
- Stabilizer: any substance which tends to keep a compound, mixture, or solution from changing its form or chemical nautre [6:964].
- Quebracho tannin: [a chemical added to boiler water.] One of its principal contributions is to keep boiler sludge fluid so that it can be carried by the circulating boiler water and more readily removed by blowdown . . . tannin decreases sludge accumulation and scale formation in the boiler . . . Tannin has as a corresive control property in that it absorbs some dissolved oxygen and, more importantly, appears to form a protective film on steel [10:258].

Description of Current Air Force Industrial Water Analysis Program

Air Force installations, as mentioned in the beginning of this study, depend on either steam or hot water to meet their heating requirements. The water in the boiler systems, through normal day-to-day loses, needs to be supplemented to maintain capacity. The water added to the system, called makeup water, is usually obtained from wells or surface water on the confines of the installation (10:254). This water is normally treated to assure that it is safe, clear, and does not emit an offensive odor or taste. Despite this treatment to drinking water standards, the water may still contain impurities which would render it unsuitable for boiler use unless further treated (10:254).

Origins of the Program

The treatments used to upgrade the water to boiler quality were adapted by the United States Bureau of Mines.

The information concerning these treatments was distributed through the use of booklets to federal heating plants (4:2). The boiler water service provided by the Bureau of Mines was the first provided by any federal agency. Manpower limitations forced the Bureau assistance to be restricted mainly to what could be accomplished by mail (4:1). AFM 85-31, Industrial Water Treatment, and AFM 85-12, Volume 1, urged the Air Force installations, with major air command approval, to use the services offered by the Bureau of Mines. The services aided in establishing the proper chemical balance of the boiler water for each system. The Bureau of Mines provided a quality control check of the on-site testing of the boiler water being done by the Air Force personnel. The Bureau provided this service to the Air Force until the end of 1981, when an independent laboratory was awarded an interim contract to provide the analysis services using the same test procedures.

In conjunction with the Bureau of Mines service, the Air Force undertook a special project with the State of Illinois. Chanute Air Force Base and Scott Air Force Base were to serve as test bases for a study that was carried out to monitor the industrial water procedures used at these installations. The study was done under the supervision of the Air Force Engineering and Services Center and was completed in 1980 (8:1). The Illinois State Water

Survey (ISWS) personnel made trips to various institutions within the State of Illinois, including the two bases mentioned, in an effort to correct any problems that were being experienced with boiler water. All of the institutions that the ISWS personnel serviced were within only a day's drive from the ISWS offices. The testing standards used by the ISWS were essentially the same as those used by the Bureau of Mines, and were again accepted by the Air Force as valid and reliable (8:1). In summary, the ISWS recommended no changes in the testing procedures, although it did recommend some changes in the treatment procedures. The testing guidelines used by ISWS and the Bureau of Mines are the basis for the tests prescribed in AFM 85-12, Volume 1.

Preservation/Stabilization Procedures Not Addressed

Specifically noteworthy to this study was the fact that neither the Bureau of Mines nor the ISWS addressed the area of sample preservation/stabilization in any of the analysis procedures for industrial water. As early as 1971, preservation procedures were available for use in preserving the phosphate constituent found in boiler-water (1:522).

The ISWS did not address the preservation/stabilization issue because of the close proximity of the service points under ISWS control. If a problem surfaced at one of the

institutions serviced by the ISWS, a team was dispatched to the site. The team would conduct an immediate analysis in an effort to discover the source of problem (9). If a more detailed analysis was required, the team collected a sample and transported the sample back to the central laboratory later the same day. The detailed analysis was conducted the next day, a schedule which prevented any serious degradation of the sample constituents from taking place (9). The Bureau of Mines, for reasons difficult to infer, chose not to pursue the idea of preservation/stabilization for the boiler-water samples that were being sent to the Bureau of Mines laboratory for analysis.

General Procedures

Generally, the industrial water used in the installations' boiler systems can either be treated prior to its injection into the system or be treated after it is in the boiler system. In either case, the water can be treated using mechanical means through the use of such procedures or devices as blowdown, steam washers, and evaporators or through the use of chemical additives to control alkalinity, scale formation, and similar problems (10:254). The initial area that is normally investigated for eliminating industrial water problems centers on maintaining a sound mechanical operating plant. In order to meet all of the industrial water treatment objectives, a mechanically sound operating plant is frequently augmented with some

type of controlled chemical treatment procedures. It is in the area of the chemical treatment of the boiler-water that the current Air Force procedures contained in AFM 85-12, Volume 1, are based. The makeup water can be chemically treated either externally or internally depending upon the size of the boiler system and the amount of makeup water required to maintain the system's requirements.

External Treatment

External treatment is divided into two categories of treatment. The first area involves using ion-exchange methods that convert the scale-forming compounds of calcium and magnesium to nonscale-forming compounds of sodium and hydrogen (10:255). The second area of external treatment involves using precipitation methods which separate the scale-forming materials from the boiler water before it is placed into the boiler system (10:255).

Internal Treatment

Many different methods are used to treat boiler-water internally. The common treatment method in the Air Force uses procedures that carefully control the alkalinity of the boiler water, add a type of alkali phosphate, and add an organic material to give the boiler water the desired characteristics that will protect the investment made in the equipment and maintain the efficiency of the system. The chemicals used for the internal boiler-water treatment

procedures are usually cheap and readily available at most Air Force installations (10:255). The boiler-water treatment provided by the chemical is controlled by the chemical's concentration and action (10:255). The chemicals commonly used for boiler-water treatment of high pressure boiler systems in the Air Force are caustic soda, sodium meta-phosphate, quebracho tannin, and sodium sulfite (if necessary) (10:255). Additional organic chemicals called amines can be added to control the corrosion in the return lines of many boiler plant systems when conditions warrant (10:255).

Functions of the Common Chemicals

The functions of these chemicals commonly used to treat Air Force industrial water are explained in the section below.

Caustic Soda:

Caustic soda provides alkalinity (causticity) in the form of free hydroxide. Causticity in boiler water serves several purposes. Primarily, it protects the boiler against corrosion by neutralizing the acids in untreated water, and it helps control scale formation. It is essential for full effectiveness of phosphate and quebracho tannin; and it is required by some neutralizing amines for good volatility with the steam. Caustic soda is not needed if the feedwater has adequate alkalinity [10:258].

Sodium Meta-phosphate:

When boiler water is treated with a phosphate chemical, the phosphate combines with calcium to precipitate calcium phosphate and is readily removed by blowdown. Since calcium phosphate is the least soluble

calcium salt that forms in boiler water, phosphate control prevents formation of calcium scales, such as calcium carbonate, calcium sulfate, or calcium silicate. However, satisfactory phosphate control requires that sufficient causticity must be maintained in the boiler. With low causticity, calcium phosphate becomes more soluble and may form a sticky sludge on boiler surfaces. Since phosphate chemicals do not decompose in the boiler, phosphate control can be used at high boiler pressures [10:258].

Quebracho tannin:

Quebracho tannin contributes to several water treatment objectives. One principal contribution is to keep sludge fluid so that it can be carried by the circulating boiler water and more readily removed by blowdown. This results from the collodial property of tannin which causes the sludge to form as finely divided particles easily borne by boiler circulation; tannin decreases sludge accumulation and scale formation in the boiler. For this reason, it is frequently used as a supplement to caustic soda treatment to enhance removal of calcium phosphate sludge. Quebracho tannin has a corrosive control property in that it absorbes some of the dissolved oxygen and, more important, appears to form a protective film on steel [10:258].

Sodium sulfite:

Improved corrosion control can be realized by applying chemical scavengers to remove the last traces of oxygen in the water remaining after mechanical deaeration. Sodium sulfite (Na₂SO₃) is the only chemical authorized for this purpose in Air Force boilers.
. . . If enough sodium sulfite is fed into a boiler, the chemical surplus maintained in the water will take up any oxygen that gets in and keep the boiler water virtually oxygen-free [10:286].

Allowable Chemical Concentrations and Immediate Testing Results

In order to maintain the proper levels of chemicals in the boiler water of the various systems, the Air Force collects samples and conducts tests on the industrial water to maintain the concentrations recommended in AFM 85-12, Volume 1. The common tests conducted at the Air Force installations are used to check the concentration of causticity, phosphate, sulfite (if used), tannin, and dissolved solids. The limits of the chemical concentration for the three areas of interest in this study are listed below.

30 to 60 parts per million (ppm) for soluble phosphate (10:266)
20 to 200 ppm for causticity, expressed as hydroxide (10:266)
20 to 40 ppm for sodium sulfite (10:287)

The schedule for the Air Force boiler water sampling and testing program is determined by the operating pressure and horsepower of the boiler systems. A highpressure, high-horsepower steam boiler (operating in excess of 15 psi and rated at 100 hp or more) must be sampled and tested daily (10:270). A high-pressure, lowhorsepower steam boiler (operating in excess of 15 psi and rates at less than 100 hp) must be sampled and tested at least twice a week and, if more than one boiler system is being used, boilers must be tested alternately (10:270). Low-pressure boiler systems (operating pressures of 15 psi or less) that are treated for corrosion should be sampled and tested at frequent intervals to maintain the desired pH tolerances between 10.5 and 11.5 (10:270). The Air Force tests used to determine the chemical concentrations are conducted at the Air Force laboratories immediately

after the samples are taken to insure the accuracy of the results.

Independent Analysis Program

As stated earlier in this report, the Air Force industrial water analysis program uses an independent laboratory as a quality control on its procedures. Samples are submitted periodically to a laboratory for independent analysis to use as a comparison with the results that were obtained from the immediate on-site testing procedures. The submission schedule for the independent sample analysis is outlined below:

I. High-Pressure Systems

- A) High-Horsepower -- Samples sent at monthly
 intervals (10:277)
- B) Low-Horsepower -- Samples sent at three-month intervals (10:278)

II. Low-Pressure Sysems

- A) Boilers treated with caustic soda
- 1. High-horsepower -- Samples sent at monthly
 intervals (10:278)
- 2. Low-Horsepower -- Samples sent at three-month
 intervals (10:278)
- B) Steel or cast iron boilers treated with caustic soda combined with meta-phosphate and tannin.

- 1. High-horsepower -- Samples sent at monthly
 intervals (10:278)
- 2. Low-horsepower -- Samples sent at three-month
 intervals (10:278)
- III. High temperature water plants (300 degrees F and greater)
 - -- Samples sent at monthly intervals (10:278)

The independent analysis program is an integral part of the Air Force industrial water analysis program.

AFM 85-31 acknowledges the importance of this independent analysis program.

The necessity of such checks has long been recognized, for they assure the plant operator of the accuracy of his tests or indicate the need for improvement [ll:p.6-1].

Cental to this research project is the fact that the time interval that normally elapses between the sample collection and testing of the sample sent to the independent laboratory is 14 days. Verification of the 14-day interval is given in Appendix B of this study, which contains the record copies of the independent laboratory results.

Independent Analysis Results and Implications

The results from the independent analysis are reported not only to the installation that submitted the samples but also to the respective major air command (ll:p.6-4). According to AFM 85-12, Volume 1, if the results of the

on-site testing vary by more that 20 percent from the independent laboratory results, a careful check of the installation's analysis procedures should be made, and the age of the installation's reagents, standard solutions, and indicators should be checked (10:278). If the installation's analysis results fail consistently to agree with the independent check analysis laboratory's results, and the local review of the abovementioned areas fails to yield the source of error or disagreement, the installation should request technical guidance from the intermediate or major command (10:278).

In summary, then, AFM 85-12, Volume 1 suggests that if a difference exists between the analysis laboratory's results and the immediate results obtained by the Air Force installations, the problem is centered at the installation level. In fact, however, this assumption is in conflict with current scientific knowledge and standard practice. Specifically, the difference could be caused by a change in the chemical composition of the sample after the sample container was sealed for shipment to the independent laboratory. The time delay between the sample collection and sample testing is, according to national standards, an important aspect that should be considered when evaluating the results of any analyses.

Description of National Standards

The national standards readily applicable to the scope of this study on industrial water analysis procedures are <u>Standard Methods</u> 14th edition and the <u>1982 Annual</u> Book of ASTM Standards, <u>Part 31</u>.

The information contained in these sources is widely accepted in the scientific community for the validity and reliability of the methods these sources contain. The preface to the 14th ed. of <u>Standard Methods</u> provides this evidence on the range of approval of its methods.

The methods presented here, as in previous editions, are believed to be best available and generally accepted procedures for the analysis of water, wastewaters, and related materials. They represent the recommendations of specialists, ratified by a large number of analysts and others of more general expertise, and as such are truly consensus standards, offering a valid and recognized basis for control and evaluation (2:v).

The foreword included in 1982 Annual Book of ASTM

Standards, Part 31 provides this support of the acceptability of its standards.

An ASTM standard represents a common viewpoint of those parties concerned with its provisions, namely, producers, users, and general interest groups. It is intended to aid industry, government agencies, and the general public. The use of an ASTM standard is purely voluntary. It is recognized that, for certain work or in certain regions, ASTM specifications may be either more or less restrictive than needed. The existence of an ASTM standard does not preclude anyone from manufacturing, marketing, or purchasing products, or using products, processes, or procedures not conforming to the standard. Because ASTM standards are subject to period review and revision, those who use them are cautioned to obtain the latest revision [3:iv].

Time Delay Problem

The topic of permissible time intervals between · water sample collection and testing is addressed specifically in Standard Methods and the 1982 Annual Book of ASTM Standards, Part 31. The shorter the interval between the collection and testing of the sample, the more reliable the analytical results will be (2:44;3:82). This is a statement that can be applied to any sample. Standard Methods states further that there exists no exact way to determine how much time can be allowed to elapse between sample collection and testing (2:44). Some constituents and physical values of a sample require that an immediate field analysis be conducted to obtain dependable results because the sample composition may change in the time required for the sample to reach the laboratory (2:44; 3:82). When the interval between sample collection and testing is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, preservation procedures should be applied if practical (2:44).

In the area of determining the soluble phosphate in the boiler-water, it is suggested by both <u>Standard Methods</u> and <u>Part 31 of ASTM</u> that the sample be tested immediately unless the sample is preserved (2:472; 3:234). Recommended preservation techniques will be discussed in a later section of this chapter (3:234).

The optimum permissible time interval specified in Standard Methods between sample collection and testing for alkalinity (causticity) is a maximum of one day in unpreserved samples (2:275). Part 31 of ASTM states that the test for causticity should be accomplished very soon after the sample is taken (3:429). Both sources state that the sample should not be allowed undue exposure to the atmosphere because chemical reactions could occur which could change the composition of the sample (2:275; 3:429).

concerning the test for sulfite, Standard Methods specifies that the test must be done immediately after collection: no delay is permissible (2:Table 105:1). Part 31 of ASTM specifies that the test for sulfite be accomplished with the minimum possible contact time between the sample and the atmosphere because of the rapid oxidation of sulfite when exposed to the air (3:595). As mentioned earlier, the time interval between sample collection and testing for the independent laboratory is normally 14 days; samples are tested immediately after collection by the Air Force at its facilities.

Preservation/Stabilization Techniques

The problem caused by the time delay between sample collection and analysis may be minimized by properly preserving/stabilizing samples prior to their being shipped to the independent laboratory. The use of

preservatives/stabilizers would retard the changes caused by chemical reactions in the composition of samples. Standard Methods states, however, that no matter what the nature of the sample, complete stability for all constituents in any one sample can never be achieved (2:43). The addition of a preservative/stabilizer may retard the change caused by one reaction, but the addition of the preservative/stabilizer itself may bring about changes that would affect the composition or the concentration of another constituent. Part 31 of ASTM specifies the chemical preservatives should be added to samples for chemical, physical, or radiological analysis procedures only as specified in the specific test method used in conducting the examination (3:82). Some constituents are more likely to be affected by the storage and transportation of the sample that may occur prior to the analysis of the sample (2:43). Some samples are unstable due to the adsorption of certain cations on, or ion exchange with, the walls of the sample container. Some properties, such as the temperature of the sample, can change quickly. The pH of the sample can change within only a few minutes, and constitutes such as ferrous and sulfite may be lost due to the oxidation reactions that occur (2:44).

Recommended Preservation/ Stabilization Techniques

Standard Methods recommends preservation of samples when tests for soluable phosphate cannot be done immediately after the sample is drawn. The standard recommends that the sample be filtered immediately and then either frozen at \leq -10C and/or 40 mg mercuric chloride/liter be added if a differentiation is to be made of the different phosphorus forms (2:Table 105:1; 3:472).

The fixing procedure that is used to stabilize the sample prior to titration for the sulfite test is described in ASTM, Part 31. The sample should be fixed by the addition of hydrochloric acid (1+1), potassium iodate solution, and 0.025N potassium iodide solution, respectively. Standard Methods states that the analysis for the sulfite constituent in the boiler water be conducted immediately since there is no known method for preservation of this constituent.

On the subject of preserving for the hydroxide or causticity value of the boiler water sample, ASTM Part 31 recommends that strontium chloride solution be added for each milligram of either carbonate or orthophosphate ion in the sample aliquot, plus a 4-ml excess. If the concentrations of the carbonate and the phosphate ion are not known, sufficient strontium chloride should be added for the highest probable amounts, since excess reagent will

not interfere except to produce turbidity that may obscure the titration end point (3:429).

These preservation/stabilization techniques were used in the experimental section of this research project, described in the next chapter.

CHAPTER II

METHODOLOGY

Chapter Overview

This chapter describes the methodology used to accomplish the research objectives and answer the research questions listed in Chapter I. It describes the daily collection and analysis routine at Wright-Patterson Air Force Base, Ohio, the experimental design that was used to verify the need for preservation/stabilization procedures, and the current test procedures used for analyzing the quantity of phosphate, sulfite, and causticity present in the sample.

Wright-Patterson Air Force Base Daily Testing Procedures

Each day at Building 770, Area B of WrightPa' erson Air Force Base, the permanent day-shift operator prepares a 1050 ml container in accordance with the procedures outlined in AFM 85-12, Volume 1. The container is opened and it is placed underneath the collection tube of the boiler's sample supply ling, where it is rinsed with the boiler water that is to be collected for the analysis. The container is allowed to fill and run over. The container is emptied and the lid of the container is rinsed

with the boiler water. At the completion of this procedure, the sample container is ready to receive the sample to be tested.

At approximately 0745 each day, the operator opens the valve of the water line for the boiler to be tested. The water line is flushed to clear the line of any stagnant water and a sample is collected in the 1050 ml plastic container. The container is closed immediately to prevent contact between the sample and the atmosphere. From this large sample, smaller portions, as prescribed in the test procedures described below, are removed and the analysis is recorded in the appropriate portion of the AF Form 1459, "Water Treatment Operating Log for Steam and Hot Water Boilers." Then, the associated laboratory equipment is thoroughly cleaned and readied for the next day's cycle of testing.

The analysis procedures from AFM 85-12, Volume 1, which are used for the on-site testing and that are pertinent to this experiment, are described below.

Phosphate Test

The standard equipment and reagents required to conduct a phosphate analysis are the following (10:272):

- 1. One phosphate color comparator block of two standards -- 30 ppm and 60 ppm of phosphate as PO_4 . (The Taylor high-phosphate slide comparator may be used instead.)
- 2. Four phosphate comparator combination tubes, each marked at 5, 15, and 17.5 ml, with stoppers.

- 3. One filter funnel, 65 mm diameter.
- 4. One package filter paper, 11 cm diameter.
- 5. One 20 ml bottle
- 6. One 1/2 ml dropper
- 7. One 1/4 teaspoon measuring spoon
- 8. Two plain test tubes, 22 mm \times 175 mm (about 50 ml capacity).
 - 9. Two rubber stoppers, No. 3
- 10. One 250 ml glass-stoppered bottle, labeled "Comparator Molybdate Reagent."
 - 11. One 32-oz bottle Comparator Molybdate Reagent
- 12. One 2-oz bottle Concentrated Stannous Chloride Reagent.
- 13. One 32-oz bottle Standard Phosphate Test Solution (45 ppm of phosphate, PO₄).

The instructions for the phosphate test procedure are as follows:

- 1. Without disturbing any settled sludge, transfer enough of the sample to a plain test tube (22 mm x 175 mm) to fill it about half.
- 2. Add 1/4 teaspoon of decolorizing carbon, stopper the tube, and shake vigorously for about one minute.
- 3. Fold a filter paper and place it in the filter funnel. Do not wet down the filter paper with water. Support the funnel if necessary to prevent jiggling. Movement may cause the sample to overflow the edge of the filter paper and drain into the tube. Filter the shaken sample, using a combination mixing tube as a receiver. Filtering is usually slow because of carbon action.
- 4. After 5 ml of sample have filtered through, as indicated by the level in the tube, discard it. Continue filtering to bring the level in the test tube again up to the 5 ml mark. The sample should come

through clear and free, or nearly free, of tannin color. If it does not, repeat the test, starting as in step (1) above. Add 1/2 teaspoon of carbon in two 1/4 teaspoon portions, and shake for a minute after each addition.

- 5. Add Comparator Molybdate Reagent to bring the level up to the second mark (15 ml). Stopper, mix by inverting the tube several times.
- 6. Add fresh dilute stannous chloride up to the third mark (17.5 ml). Stopper, mix by inverting. If phosphate is present, the solution in the mixing tube turns blue.
- 7. Place the tube in the comparator block. About one minute later compare the color of the solution in the tube with the standard colors of the phosphate color block. Colors between the two standard colors may be estimated. Do not allow test to stand for more than five minutes because the color fades rapidly.
- 8. Record the results in the appropriate column on AF Form 1459, "Water Treatment Operating Log for Steam and Hot Water Boilers" (para 313) as low, if below 30 ppm; high, if above 60 ppm; OK, if between 30 and 60 pmm [10:pp. 272-273].

Sulfite Test

The standard equipment and reagents required to conduct a sulfite analysis are the following (10:275).

- 1. Two marked test tubes
- 2. Two plain test tubes
- One stopper for plain test tube
- 4. One stirring rod
- 5. One 7-inch dropper
- 6. One 1/4 teaspoon
- 7. One 50 ml beaker
- 8. One 150 ml beaker

- 9. One 20 ml acid dropping bottle, with dropper marked at 1/2 ml for 3N hydrochloric acid.
- 10. One 20 ml starch dropping bottle, with dropper marked at 1/2 ml for starch indicator.
 - 11. One 2-oz bottle of potato or arrowroot starch
 - 12. One 8 ml vial of thymol
 - 13. One 32-oz bottle of 3N hydrochloric acid
- 14. One 1-pt amber bottle of standard potassium
 iodate-iodide reagent.

The instructions for the sulfite test procedure are as follows:

- 1. Using the appropriate instrument, transfer two $1/2\ \text{ml}$ portions of 3N hydrochloric acid to a clean, marked test tube.
- 2. From the starch solution, transfer $1/2\ ml$ of starch to the marked test tube with the acid.
- 3. Without disturbing any settled sludge in the sample, add enough sample to bring the level in the tube up to the first mark (25 ml).
- 4. Transfer enough standard potassium iodateiodide reagent from the stock bottle to fill a 7-inch dropper.
- 5. Add the reagent to the mixture, a drop at a time, counting the drops and stirring after each drop is added, until the mixture turns blue and stirring no longer removes the color.
- 6. Figure the sodium sulfite concentration in the boiler water by multiplying the total drops used minus 1 by 5. Each drop indicates 5 ppm of sodium sulfite except the last drop.
- 7. Record test results as ppm on the AF Form 1459, "Water Treatment Operating Log for Steam and Hot Water Boilers" [10:276].

Causticity Test

The standard equipment and reagents required to conduct a causticity analysis are the following (9:270):

- 1. Two 8-inch droppers with bulbs.
- 2. Two 250 ml stoppered bottles, labeled "Causticity Reagent No. 1" and "Causticity Reagent No. 2."
 - 3. Four marked test tubes, 22 mm x 185 mm.
 - 4. Three plain test tubes, 22 mm x 175 mm.
 - 5. Two rubber stoppers, No. 3.
 - 6. One 14-inch test tube brush.
 - 7. One test tube clamp.
 - 8. Two 9-inch stirring rods.
- 9. One 1-oz indicator dropping bottle for phenol-phthalein.
 - 10. One test tube rack.
 - 11. One quart bottle Causticity Reagent No. 1.

The instructions for this procedure are as follows:

- 1. Without disturbing any settled sludge, fill a marked test tube exactly to the first mark (25 ml) with the original boiler-water sample.
- 2. Shake Causticity Reagent No. 1 (barium chloride solution saturated with phenolphthalein) thoroughly and add enough to bring the level in the tube exactly to the second, or long, mark (30 ml). Stir the solution with the stirring rod, which must be kept clean and reserved for the causticity test only. If the mixture remains colorless or does not turn pink, the causticity in the boiler water is zero and the test is finished.
- 3. If the mixture turns pink, causticity is present. (If pink color is not very deep, intensify it by adding two drops of phenolphthalein indicator to the

mixture in the tube). Add Causticity Reagent No. 2 (standard 1/30 normal acid), using the clean 8-inch dropper reserved for the causticity test only. To add Causticity Reagent No. 2, draw it from the reagent bottle into the dropper with the rubber bulb, and add it drop by drop, to the test tube. After each addition, stir the mixture with a stirring rod. When sufficient reagent has been added, the pink color disappears; usually the change point is very sharp. As soon as the pink color just fades out, stop adding reagent.

- 4. The amount of Causticity Reagent No. 2 required to make the pink color disappear indicates the concentration of hydroxide (OH) or causticity in the boiler water. The amount of reagent used is shown by the marks on the test tube above the long mark (30 ml). The distance between any two marks on the test tube equals 5 ml; readings less than 5 ml can be estimated. For example, if only 3/5 of the distance between the long mark and the mark above was filled, then 3 ml were added. If the distance filled was past one mark plus 3/5 of the distance to the next, then 5+3=8 ml were used. To obtain the actual ppm of the hydroxide or causticity shown by the test, multiply the number of ml by 23. Thus, for 8 ml of Causticity Reagent No. 2 there are 8 x 23 = 184 pmm hydroxide or causticity in the water.
- 5. Record the results of the test in the proper column of AF Form 1459, "Boiler Water Treatment Operating Log" (see para 313) [10:pp. 270-271].

These three procedures were used in the experiment described below.

Experimental Procedure

The experiment on preservation reported in this study involved the high pressure steam boiler systems that are in Building 770, Area B, at Wright-Patterson Air Force Base. Although only one installation was used in this experiment, the conclusions obtained will be applicable to the other Air Force installations because all of the installations must follow the procedures outlined above.

This experiment augmented the normal daily routine described earlier in this chapter for Wright-Patterson Air Force Base. "It was repeated daily for 20 days.

Experimental Data Collection

Drawing the Experimental and Control Samples

Three 1050 ml samples were drawn at 0750 each day of the experiment. The samples were collected in containers that had been rinsed in boiler water. Each of the three daily samples was assigned to one of the groups described in the next section.

Group Divisions

Three groups were created in which samples could be placed. The first group, the control group, contained those 1050 ml samples that were used for the immediate onsite testing procedures conducted daily by the permanent day shift boiler operator. The second group, the preserved/stabilized group, contained the 1050 ml samples that were used for the preservation variable of the experiment. The third group, the unpreserved group, contained the 1050 ml unpreserved samples that were analyzed after a specified time period described later in this chapter.

Assigning Group Divisions

To provide random samples to use in the experiment, a method was devised that used a random number

generator and a matrix of the permutations of the numbers 1, 2, and 3, to select a 1050 ml container that would be used for the preservation/stabilization aspect of the experiment and to select the order in which the preserved/stabilized samples were drawn from the selected 1050 ml sample assigned to the preserved/stabilized group.

First, a random number generator was used in choosing which of the three 1050 ml samples would be used for the preserved/stabilized sample. A number between one and three was randomly selected using the "S" program on the VAX 11/780 computer. If the generator selected the number one, the first sample drawn from the boiler-water sample supply line was assigned to the preserved/ stabilized group. The remaining samples were used to fill the other two groups. If the generator selected the number two, the second 1050 ml sample drawn from the boiler water sample supply line was assigned to the preserved/stabilized group and similarly, if the random number generator selected the number three, the third 1050 ml sample drawn from the boiler water sample supply line would be assigned to the preserved/stabilized group.

Once the particular 1050 ml sample was selected to be preserved/stabilized, the order in which the smaller samples were drawn from this 1050 ml sample for the preservation/stabilization procedures outlined in

Chapter I, was randomly established by a process similar to that used to select the 1050 ml sample. Since this experiment is centered on three test procedures, those for the phosphate, sulfite, and causticity constituent, a preserved/stabilized sample for each constituent was obtained each day. To insure a random order was used in drawing these three samples from the selected 1050 ml container, a random number generator was used in conjunction with a 6x3 matrix containing the six possible permutations of the numbers 1, 2, and 3. A number between one and six was randomly selected using the "S" program on the VAX 11/780 computer.

A copy of the selection table, showing the selection of 1050 ml sample container for the preservation/ stabilization procedures and the order in which the preserved/stabilized samples were drawn from the selected 1050 ml container is shown in Table 2.1.

Group Processing Procedures

The three 1050 ml daily samples were processed according to the following procedures. As previously stated, the control group received no preservatives and was tested immediately by the permanent day shift operator in accordance with AFM 85-12, Volume 1.

For the preserved/stabilized group, the 1050 ml sample was distributed into three 125 ml aliquots, placed in separate containers. Cnce the samples were in the 125 ml

containers and the random order for the preservation/
stabilization was run, the respective preservative/
stabilizing agents were added to the samples
as specified by the national standards discussed in
Chapter I. After the preservatives/stabilizers were
added, the 125 ml sample containers were sealed and stored
for a 14-day time interval before they were analyzed. The
storage conditions will be discussed later in this
chapter. On the fifteenth day after collection and
preservation/stabilization, each preserved/stabilized
sample was analyzed according to the procedures specified
in AFM 85-12, Volume 1.

The unpreserved group, like the control group, received no preservatives/stabilizers. Once the 1050 ml sample was drawn, the container was sealed and stored under the same conditions as the preserved/stabilized group.

Labeling

The labeling of the samples was kept simple. Each sample container label contained the date and time the sample was taken and the boiler that was tested. The preserved/stabilized samples had their respective container labels annotated with the name of the constituent for which the sample was preserved/stabilized.

TABLE 2.1
SELECTION AND ORDER OF PRESERVED SAMPLES

Day Sample Collected	1050 ml Container Selected For Preservation/ Stabilization	Order of Preserved/Stabilized Sample		
		Phosphate	Sulfite	Causticity
1 2 3	3 1 3	3 2 2	2 3 1	1 1 3
4 5	3 1	1	3 3	2 2
6 7 8 9 10	2 2 2 2 1	1 1 3 2 3	3 2 2 3 2	2 3 1 1
11 12 13 14 15	2 2 3 2 1	3 1 3 3	1 3 2 2 2	. 2 2 1 1 3
16 17 18 19 20	2 2 2 2 2	1 2 1 2 2	2 1 3 1 3	3 3 2 3 1

Storage Conditions

The storage conditions under which the preserved/
stabilized and the unpreserved group samples were kept
simulated the conditions under which the samples were normally sent to the independent laboratory. Once the
samples were drawn, the preservative/stabilizer added to
the preserved/stabilized samples, and the containers
sealed and labeled, the sample containers were placed in a
box to prevent light from shining on the containers. The
boxes with the containers inside were placed on a shelf
and allowed to stand until the end of the day
(approximately 4 hours) to simulate the time and conditions that occurred from the time the sample was drawn
until it is picked up for mailing.

At the end of the day, the boxes were placed in the trunk of an automobile to simulate the agitation and temperature conditions the samples undergo during transit to the independent lab. At the end of four days, the estimated normal transit time, the boxes were removed from the vehicle and placed on a shelf in the boiler plant during the remainder of the fourteen-day time interval until they were removed for analyses.

Number of Samples

In total, one hundred samples were taken during the course of the experiment. The subtotals are as follows:

- 20 -- 125 ml samples were preserved for phosphate analysis.
- 20 -- 125 ml samples were stabilized for sulfite analysis.
- 20 -- 125 ml samples were preserved for causticity analysis.
- 20 -- 1050 ml unpreserved samples were used for the immediate testing procedures.
- 20 -- 1050 ml unpreserved samples were used for the delayed complete analysis procedures after the fourteen-day interval elapsed.

Record Keeping

Tables were created in which the results of the five daily samples were recorded. Table 2.2 illustrates a sample daily table.

Gradient Delay Analysis

In order to illustrate the effect of time as a single variable on unpreserved boiler water samples, seven additional unpreserved 1050 ml samples were collected. Once the samples were drawn, the containers were sealed and placed on a shelf inside a cabinet in Building 770. The effect of time on the samples was examined by selecting one of the seven containers every 48 hours (total of 14 days) and conducting a complete analysis for phosphate, sulfite, and causticity. The results are presented in Chapter III of this study.

TABLE 2.2

SAMPLE TESTING RESULTS (Dated Collected Time

			Result	Results of Analysis (ppm)	(wdd)
Constituent Tested	Preserved/ Stabilized	Date Analyzed	Phosphate	Sulfite	Causticity
Phosphate	Yes	×	×	1	;
Sulfite	Yes	×	;	×	;
Causticity	Yes	×	1	ŀ	×
All (Immediate Test)	No	×	×	×	×·
All (Delayed Test)	No	×	×	×	×

Analyzing the Data

when the results of all daily tests had been assembled, a comparison was made between the proserved/ stabilized group and the control group and between the unpreserved group and the control group by comparing the differences between the results of the various groups with respect to the 20 percent maximum limit stated in AFM 85-12, Volume 1. The results of the chemical analyses and comparisons are presented in Chapter III.

CHAPTER III

RESULTS

Chapter Overview

This chapter presents the sample test results for the phosphate, sulfite, and causticity constituents that were obtained during the 20 days of the experiment and a comparitive analysis of the findings. Also included in this chapter are the results of the gradient delay analysis and the associated plots for the three constituents analyzed. An analysis and discussion of these results are presented in Chapter IV.

Presentation of Findings

Daily Sampling Analysis Results

Tables 3.1 thru 3.3, presented in this section of the study, contain a summary of the results of the analyses that were conducted on the immediate testing (control), the preserved/stabilized, and the unpreserved groups. The control group samples were analyzed for phosphate, sulfite, and causticity immediately after the sample was collected. The preserved/stabilized and unpreserved group samples were analyzed after the 14-day time interval for

TABLE 3.1

SAMPLE TESTING RESULTS SUMMARY FOR PHOSPHATE (ppm)

Day of Experiment	Control Group	Preserved/ Stabilized Group	Unpreserved Group
1 2 3 4 5	1 1 1 30	1 1 1 1 25	1 1 1 20
6 7 8 9 10	30 30 35 35 20	29 20 25 35 20	25 20 25 35 15
11 12 13 14 15	30 40 15 15 13	28 40 15 15	25 35 15 12 15
16 17 18 19 20	15 15 30 15 15	15 15 30 15 15	15 15 25 12 15

TABLE 3.2
SAMPLE TESTING RESULTS SUMMARY
FOR SULFITE (ppm)

Day of Experiment	Control Group	Preserved/ Stabilized Group	Unpreserved Group
1	45	5	40
2	60	10	55
1 2 3 4	35	5 5 5	25
4	20	5	10
5	65	5	50
6	105	20	75
7	30	10	25
6 7 8 9	70	10	45
9	75	15	65
10	230	20	150
11	205	15	85
12	45	15	30
13	25	15	15
14	85	15	60
15	25	5	20
16	40	15	45
17	145	35	145
18	95	70	75
19	25	15	10
20	75	75	85

TABLE 3.3

SAMPLE TESTING RESULTS SUMMARY FOR CAUSTICITY (ppm)

			
Day of	Control	Preserved/ Stabilized	Unpreserved
Experiment	Group	Group	Group
			
_			
1	90.6	87.4	94.3
1 2 3	126.5	117.3	126.5
3	117.3	103.5	110.4
4	115	94.3	110.4
5	218.5	196.8	211.6
6	299	282.9	299
7	200.1	142.6	197.8
8	154.1	115	158.7
9	167.9	112.7	165.6
10	78.2	69	87.4
10	70.2	09	0/.4
11	119.6	66.7	87.4
12	177	119.6	172.5
13	267	239.2	269.1
14	142.6	119.6	147.2
15	181.7	147.2	174.8
16	170.2	131.1	161
17	207	177.1	204.7
18	230	184	218.5
19			
	184	147.2	200.1
20	177.1	138	174.8

the same constituents that were analyzed in the control group. The complete analysis results are contained in Appendix D of this study.

Comparison of Results for the Daily Analyses

From the results of the daily analyses contained in Tables 1 thru 20, Appendix D, the differences between the preserved/stabilized group and the control (immediate testing) group results were calculated. Also, the differences between the unpreserved group and the control group results were calculated. Once the differences were obtained, a comparison of these findings was made to see if the 20 percent maximum limit specified in AFM 85-12, Volume 1, and discussed in Chapter I, was exceeded. The raw data for this comparison is presented in Appendix E. The overall results are the following:

The difference between the preserved/stabilized group and the control group for the phosphate constituent exceeded the 20 percent maximum on 2 of the 20 days of the experiment. The difference between the unpreserved group and the control group for the phosphate constituent exceeded the 20 percent maximum limit on 4 of the 20 days of the experiment.

The difference between the preserved/stabilized group and the control group for the sulfite constituent exceeded the 20 percent maximum limit on 19 of the 20 days

of the experiment. The difference between the unpreserved group and the control group for the sulfite constituent exceeded the 20 percent maximum limit on 12 of the 20 days of the experiment.

Finally, the difference between the preserved/
stabilized group and the control group for the causticity
constituent exceeded the 20 percent maximum limit on 7 of
the 20 days of the experiment. The difference between the
unpreserved group and the control group exceeded the 20
percent maximum on 1 of the 20 days of the experiment.

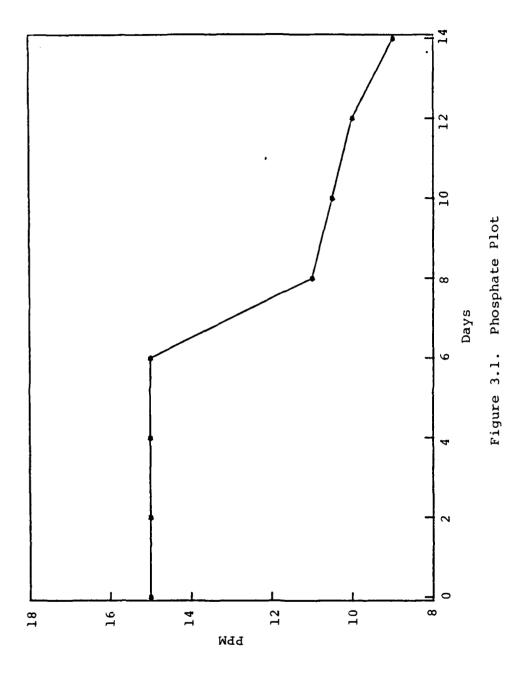
Gradient Delay Analysis Results

Table 3.4 contains the results of the analyses that were conducted every 48 hours on the 7 samples drawn from boiler #1, housed in Building 770, on 7 July 1983. These analyses were used to illustrate the time delay effect on the phosphate, sulfite, and causticity constituents normally found in boiler #1. Following the presentation of these results, the plots of the various constituents with respect to time are presented in Figures 3.1 through 3.3, which give a visual presentation of the time delay effect.

TABLE 3.4

GRADIENT DELAY ANALYSIS RESULTS
(Date Drawn: 7 July 1983; Boiler Tested: #1; Time: 0749)

	Concentration (ppm)		
Date Analyzed	Phosphate	Sulfite	Causticity
Immediate	15	160	138
9 July	15	195	140.3
ll July	15	190	144
13 July	15	170	144
15 July	11	155	138
17 July	10.5	150	133.4
19 July	10	145	133.4
21 July	9	145	133.4



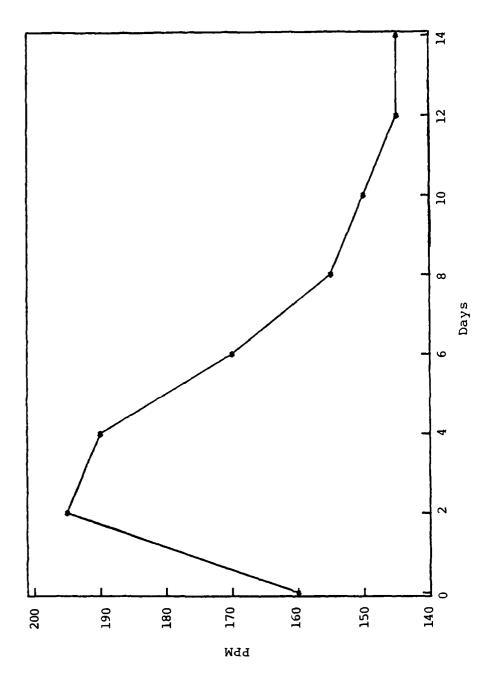


Figure 3.2. Sulfite Plot

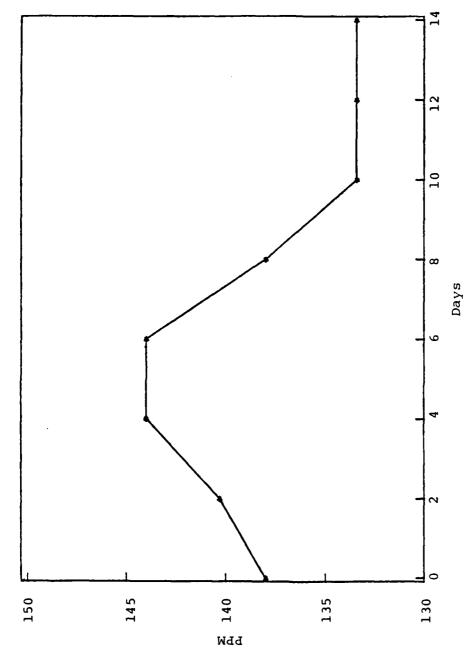


Figure 3.3. Causticity Plot

CHAPTER IV

ANALYSIS AND DISCUSSION

Chapter Overview

This chapter contains the analysis of the data collected during the daily sample testing procedures that were outlined in Chapter II. The testing results for the phosphate, sulfite, and the causticity constituents are analyzed separately, using the comparison of the result differences to the 20 percent limit described in Chapter I. Also discussed in this chapter are the results obtained during the gradient delay procedures.

Analysis of Daily Sample Data

Phosphate Constituent

The data collected on the phosphate constituent tested in this study resulted in the following values:

10 percent (2 out of 20) of the differences in results between the preserved phosphate group and the phosphate control group exceeded the 20 percent limit.

20 percent (4 out of 20) of the differences in results between the unpreserved phosphate group and the phosphate control group exceeded the 20 percent limit.

The results obtained from the comparisons were in fact similar. The results of the daily testing procedures indicate that despite the use of preservation techniques the concentration of the phosphate constituent did in fact change during the course of the 20 day experimental portion of this study.

Sulfite Constituent

The data collected on the sulfite constituent was recorded even though the samples were in fact only stabilized for titration and not preserved as had been the phosphate constituent discussed earlier in this chapter.

Analysis of the data yielded the following values:

95 percent (19 out of 20) of the differences between the results of the stabilized sulfite group and the sulfite control group exceeded the 20 percent maximum limit.

60 percent (12 out of 20) of the differences between the results of the non-stabilized sulfite group and the sulfite control group exceeded the 20 percent maximum limit.

The results obtained from these comparisons varied greatly from those obtained from the analysis of the phosphate groups. However, these results also indicate that the stabilization procedures did not prevent constituency changes.

Causticity Constituent

The data collected on this constituent resulted in the following values:

35 percent (7 out of 20) of the differences between the results of the preserved causticity group and the causticity control group exceeded the 20 percent maximum limit.

5 percent (1 out of 20) of the differences between the results of the unpreserved causticity group and the causticity control group exceeded the 20 percent maximum limit.

The results obtained from the comparisons were similar to but not of the same magnitude as the results obtained in the daily sampling testing results for the sulfite constituent. These results again indicated that the preservation procedures were not effective in preventing constituency changes.

In summary, the results gathered from the analysis of the phosphate, sulfite, and the causticity constituents illustrate that preservation/stabilization techniques are not effective in preventing constituency changes as indicated by <u>Standard Methods</u> and <u>ASTM Part 31</u>. The results further illustrate the effect that a time delay has on the analysis results.

Analysis of Gradient Delay Data

Gradient Phosphate Results

The objective of doing the gradient delay analysis using the testing procedures outlined in Chapter II was to illustrate what effect time had on the three constituents examined in this study. The values obtained for the phosphate analysis of the gradient samples are presented

in Table 3.4 and graphically portrayed in Figure 3.1. They clearly show the effect that a time delay had on the phosphate constituent. It is not relevant to this study whether the concentration of the phosphate went up or down but that a change took place during the 14-day time interval between the collection and analysis of the sample. The concentration of the phosphate was initially 15 ppm on Day 0, and was still decreasing on Day 14 with a value of 9 ppm.

Gradient Sulfite Results

By the test procedures outlined in Chapter II, the values obtained for the concentration of the sulfite constituent recorded in Table 3.4 and graphically presented in Figure 3.2 illustrate that a time delay also affects the concentration of the sulfite constituent present in the boiler water tested. The concentration on Day 0 was 160 ppm and on Day 14 the concentration decreased to 145 ppm.

Gradient Causticity Results

The testing procedures outlined in Chapter II for the causticity analysis provided the results for the concentration of the causticity constituent contained in Table 3.4 and graphically presented in Figure 3.3. The results illustrate that a time delay also affects the

results of the causticity analysis. As mentioned before, it is not important whether the value for causticity went up or down, but that a change in the concentration of the causticity value occured at all. The causticity value was initially 138 ppm on Day 0 and it decreased to 133.4 ppm on Day 14 of the analysis period used in the gradient delay procedures.

In summary, this analysis further indicates that sample constituency changes with time. The recommendations of this study in light of both the comparison of results for the daily sample analyses and the gradient time delay analysis results will be presented in the next chapter.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Chapter Overview

This chapter summarizes the conclusions that can be drawn from this study on the three constituents of boiler water: phosphate, sulfite, and causticity. Recommendations upon which to base improvements to the existing Air Force industrial water analysis program are made, and recommendations for further research are suggested.

Specific Conclusions

Phosphate Determination

The results of the comparisons made on the daily sample testing results indicate that the preservation technique used for the phosphate constituent was not effective in preventing changes in the concentration of the phosphate.

The results obtained through the gradient delay analysis was effective in showing that the concentration of the phosphate constituent did change during the time interval between sample collection and analysis. The

results of the daily samples analyses also showed the change in the phosphate concentration over the same 14-day time delay period, despite the application of a preservative.

The analysis of the phosphate constituent lends evidence that would reaffirm the national standards statement that the on-site/field analysis of the boiler water yields results which more accurately reflect the concentrations of the various constituents that were present at the time of sampling, because of the changes which can occur between sample collection and analysis.

Sulfite Determination

The results of the comparisons made on the daily sample testing results indicate that the stabilization procedure used for the sulfite constituent was not effective in preventing changes in the concentration of the sulfite. A total of 95 percent of the stabilized group was outside the 20 percent limit. The results of the unpreserved group were, in ract, not that much better, with 55 percent of the differences outside of the 20 percent limit.

The results obtained from the gradient delay analysis for sulfite provided similar evidence to the information from the gradient delay analysis conducted on the phosphate constituent. The concentration of the sulfite

constituent does, in fact, change over the 14-day time delay period.

This sulfite analysis, like the phosphate analysis reported earlier in this chapter, provides evidence that the immediate on-site/field analysis of the boiler water yields a more accurate representation of the concentration of constituents present in the boiler water as stated in the national standards.

Causticity Determination

The results of the comparative analysis of the causticity constituent were parallel to the results reported for the sulfite constituent except in the magnitude of the number of observations that were outside of the 20 percent limit. Only 35 percent of the preserved group versus control group results were outside of the 20 percent limit and only 5 percent of the unpreserved group versus control group results were outside the 20 percent.

The gradient delay analysis for the causticity provided information that was similar to the information presented for the phosphate and sulfite. The concentration of the causticity constituent did, in fact, change during the 14-day time delay period.

In summary, none of the preservation/stabilization procedures used for the constituents examined in this study prevented changes in the constituent concentrations

during the 14-day time delay interval. In fact, in the case of the sulfite constituent, the stallization process generated results that were worse than if nothing at all had been done to the samples. The one fact that was consistent throughout the experiment was that the concentrations of all of the constituents examined changed during the 14-day time delay interval. This fact reaffirms the national standard statements that the immediate on-site/field analyses provided the most accurate results of the boiler water composition.

The samples received by the independent laboratory are not representative of the actual boiler water sample at the time it was drawn. The recommendations that the independent laboratory makes based on the unrepresentative samples could cause a waste of chemicals or result in damage to the boiler system equipment.

Recommendations

The recommendations of this study for the current Air Force industrial water analysis program and for further research are the following:

- 1. It is recommended that preservation/ stabilization procedures not be incorporated in the Air Force industrial water analysis program.
- 2. It is recommended that the current independent analysis program be eliminated. The samples received by

the independent laboratory are not representative of the actual boiler water sample at the time it was drawn.

- 3. A program should be established in which an independent laboratory would send standard test solutions to those bases with boiler water systems to be analyzed by the on-site boiler operator. The results obtained by the on-site operator would be reviewed by the independent laboratory as a quality control check on the on-site industrial water analysis procedures and recommendations to correct any analysis problems would be provided to the respective bases. As an alternative to this suggestion, a program could be established that would pattern its operations after the procedures that were worked out between the Air Force and the Illinois State Water Survey personnel. A laboratory in close proximity to the installation involved could provide the consulting service and conduct the necessary analyses on-site without incurring a large time delay between sample collection and analysis.
- 4. It is a recommendation of this author that a cost analysis be done to determine the feasibility of instituting the programs outlined in recommendation 3 of this study.
- 5. It is further recommended in this study that the Air Force rely on the results of the on-site analysis results when making changes to the chemical concentrations

required to maintain the boiler systems within the specified limits outlined in AFM 85-12, Volume 1.

6. For additional study, an experiment can be conducted in which the base laboratory could take a number of identical samples and conduct an immediate analysis on one-third of the samples for phosphate, sulfite, and causticity; store one-third of the samples; and send one-third of the samples to the independent laboratory for analysis. On the same day that the independent laboratory is starting its analysis of the samples, the independent lab should call the base and notify the personnel so the base can start its analysis on the stored samples at approximately the same time. Once the analyses are completed, all of the results should be sent to the researcher so that a statistical analysis can be conducted as further confirmation that delayed analysis is not representative of field conditions.

APPENDICES

APPENDIX A

DIFFERENCES BETWEEN THE AIR FORCE RESULTS AND THE INDEPENDENT LABORATORY RESULTS

Date Drawn: 22 Sep 82; Date Analyzed: 7 Oct 82; Boiler Tested: #4

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate	15	3.6	76
Sulfite	14	3	78.57
Causticity	160	174	- 8.75

Date Drawn: 13 Nov 82; Date Analyzed: 24 Nov 82; Boiler Tested: #4

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate Sulfite	45 30	56 27	-24.4 10
Causticity	142	128	9.86

Date Drawn: 6 Dec 82; Date Analyzed: 17 Dec 82; Boiler Tested: #5

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate	50	2.9	94.2
Sulfite	50	2	96
Causticity	230	137	40.43

Date Drawn: 17 Jan 83; Date Analyzed: 2 Feb 83; Boiler Tested: #4

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate	30	<1	96.7
Sulfite	40	17	57.5
Causticity	230	138	40

Date Drawn: 24 Mar 83; Date Analyzed: 8 Apr 83; Boiler Tested: #4

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate	30	15	50
Sulfite	55	<2	96.4
Causticity	181	201	-11.05

Date Drawn: 2 Apr 83; Date Analyzed: 3 May 83; Boiler Tested: #5

Concentration (ppm)

Constituent	Immediate Test	Independent Lab Test	Percent Difference
Phosphate	45	14.8	67.1
Sulfite	30	<2	93.3
Causticity	161	197	-22.4

APPENDIX B

VERIFICATION OF 14-DAY TIME INTERVAL

LAB # 82-09-123	DENTIFICATION	NOIL		used on this report		
11 SETV KEPURI 10/07/82 10:45:18	PREPARED DY ATTEN I DENTIF	INFORMATION		Analytical Serv TEST CODES and NAMES used on this report	Hardness Bicarbonate Specific Conductance	111 A RH PO4 B PUSPhate 503 TA Sulfite
PAGE 1 Analytical Serv RECEIVED: 09/27/82 10/0	REPORT 2750th CES TO DEMNIB Wright-Patterson AFD Dayton, OH 45433 ATTEN Clyde Farris	CLIENT AFB W PATT B SAMPLES I COMPANY USAF FACILITY WIGHT-Patterson AFB	WORK ID <u>Boiler Water Analysis</u> TAKEN <u>9-22-82</u> TRANS <u>US Priority Mail</u> TYPE <u>boiler water</u> P. O. # <u>204-006-70-01</u> INV. # <u>82090337</u>	SAMPLE IDENTIFICATION Analytication Cont. Blowdown	1003 A PUCOS A	FOR B FOR B SIGN TA

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APPENDIX C

COMPUTER LISTING OF "S" PROGRAM FOR RANDOMIZATION PROCEDURES

This program is used to generate Table 2.1 for the selection and order of the preserved samples.

Matrix created using the permutations of the numbers 1, 2, 3.

pmat_matrix(c(1,2,3,1,3,2,2,1,3,2,3)
1,3,2,1,3,1,2),6,3,byrow=TRUE)

nctivity is conducted for 30 days
for(day in 1:30)

The 1050 ml container is selected for preservation.

vile_round(runif(tv1,3))

The Table 2.1 is generated binding the permutations with the selected 1050 ml vile.

perm_c(vile,pmatEround(runif(1.1.6)),1)
print ("day is ",day."use ",perm);

APPENDIX D

DAILY SAMPLE TESTING RESULTS

TABLE 1

SAMPLE TESTING RESULTS
(Date Collected: 9 Jul 83; Time: 0745)

			Results	of Analy	rsis (ppm)
Constituent Tested	Preserved/ Stabilized	Date Analyzed	Phos- phate	Sul- fite	Caus- ticity
Phosphate	Yes	24 July	1		
Sulfite	Yes	24 July		45	
Causticity All	Yes	24 July			87.4
(immediate test)	No	9 July	1	45	90.6
(delayed test)	No	24 July	1	40	94.3

TABLE 2

SAMPLE TESTING RESULTS
(Date Collected: 10 Jul 83; Time: 0745)

Constituent Tested	Preserved/ Stabilized		Results	of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	25 July	1			
Sulfite	Yes	25 July		55		
Causticity All	Yes	25 July			117.3	
(immediate test)	No	10 July	1	60	126.5	
(delayed test)	No	25 July	1	55	126.5	

TABLE 3

SAMPLE TESTING RESULTS
(Date Collected: 11 Jul 83; Time: 0748)

Constituent Tested	Preserved/ Stabilized	Results		of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	26 July	1			
Sulfite	Yes	26 July		5		
Causticity All	Yes	26 July			103.5	
(immediate test)	No	ll July	1	35	117.3	
(delayed test)	No	26 July	1	25	110.4	

TABLE 4

SAMPLE TESTING RESULTS
(Date Collected: 12 Jul 83; Time: 0743)

Constituent Tested	Preserved/ Stabilized		Results	of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	27 July	1			
Sulfite	Yes	27 July		5		
Causticity All	Yes	27 July			94.3	
(immediate test)	No	12 July	1	20	115	
(delayed test)	No	27 July	1	10	110.4	

TABLE 5

SAMPLE TESTING RESULTS
(Date Collected: 13 Jul 83; Time: 0744)

•			Kesults	or Analy	rsis (ppm)
Constituent Tested	Preserved/ Stabilized	Date Analyzed	Phos- phate	Sul- fite	Caus- ticity
Phosphate	Yes	28 July	25		
Sulfite	Yes	28 July		5	
Causticity All	Yes	28 July			196.8
(immediate test)	No	13 July	30	60	218.5
(delayed test)	No	28 July	20	50	211.6

TABLE 6

SAMPLE TESTING RESULTS
(Date Collected: 14 Jul 83; Time: 0746)

Constituent Tested	Preserved/ Stabilized		Results	of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	29 July	29			
Sulfite	Yes	29 July		20		
Causticity All	Yes	29 July			282.9	
(immediate test)	No	29 July	30	105	299	
(delayed test)	No	29 July	25	75	299	

TABLE 7

SAMPLE TESTING RESULTS
(Date Collected: 15 Jul 83; Time: 0745)

Constituent Tested	Preserved/ Stabilized		Results	of Analy	f Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity		
Phosphate	Yes	30 July	20				
Sulfite	Yes	30 July		10			
Causticity All	Yes	30 July			142.6		
(immediate test)	No	15 July	30	30	200.1		
All (delayed test)	No	30 July	20	25	197.8		

TABLE 8

SAMPLE TESTING RESULTS
(Date Collected: 16 Jul 83; Time: 0750)

Constituent Testea	Preserved/ Stabilized		Results	of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	31 July	25			
Sulfite	Yes	31 July		10		
Causticity All	Yes	31 July			115	
(immediate test)	No	16 July	35	70	154.1	
(delayed test)	No	31 July	25	45	158.7	

TABLE 9

SAMPLE TESTING RESULTS
(Date Collected: 17 Jul 83; Time: 0750)

Constituent Tested	Preserved/ Stabilized	Result			of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity		
Phosphate	Yes	l Aug	35				
Sulfite	Yes	1 Aug		15			
Causticity All	Yes	1 Aug			112.7		
(immediate test)	No	17 July	35	75	167.9		
(delayed test)	No	1 Aug	35	65	165.6		

TABLE 10

SAMPLE TESTING RESULTS
(Date Collected: 18 Jul 83; Time: 0750)

Constituent Tested	Preserved/ Stabilized	Result		s of Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	2 Aug	20			
Sulfite	Yes	2 Aug		20		
Causticity All	Yes	2 Aug	~-		69	
(immediate test)	No	18 July	20	230	78.2	
(delayed test)	No	2 Aug	15	150	87.4	

TABLE 11

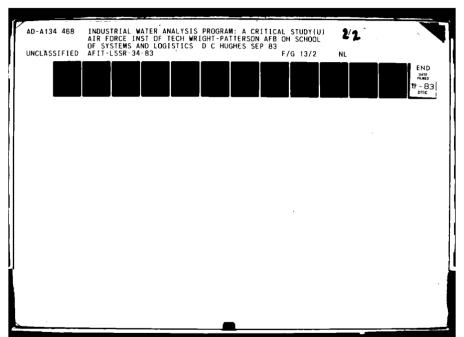
SAMPLE TESTING RESULTS
(Date Collected: 19 Jul 83; Time: 0750)

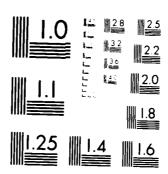
Constituent Tested				Results of Analysis (ppm)		
	Preserved/ Stabilized	Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	3 Aug	28			
Sulfite	Yes	3 Aug		15		
Causticity All	Yes	3 Aug			66.7	
(immediate test)	No	19 July	30	205	119.6	
(delayed test)	No	3 Aug	25	85	87.4	

TABLE 12

SAMPLE TESTING RESULTS
(Date Collected: 20 Jul 83; Time: 0747)

Constituent Tested	Preserved/ Stabilized		Results	of Analysis (ppm)	
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity
Phosphate	Yes	4 Aug	40		
Sulfite	Yes	4 Aug		15	
Causticity All	Yes	4 Aug			119.6
(immediate test)	No	20 July	40	45	177
(delayed test)	No	4 Aug	35	3 0	172.5





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TABLE 13

SAMPLE TESTING RESULTS
(Date Collected: 21 Jul 83; Time: 0751)

Constituent Tested	Preserved/ Stabilized		Results	of Analy	Analysis (ppm)		
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity		
Phosphate	Yes	5 Aug	15				
Sulfite	Yes	5 Aug		15			
Causticity All	Yes	5 Aug			239.2		
(immediate test)	No	21 July	15	25	267		
(delayed test)	No	5 Aug	15	15	269.1		

TABLE 14

SAMPLE TESTING RESULTS
(Date Collected: 22 Jul 83; Time: 0743)

Constituent Tested		Date Analyzed	Results of Analysis (ppm)			
	Preserved/ Stabilized		Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	6 Aug	15			
Sulfite	Yes	6 Aug		15		
Causticity All	Yes	6 Aug			119.6	
(immediate test)	No	22 July	15	85	142.6	
(delayed test)	No	6 Aug	12	60	147.2	

TABLE 15

SAMPLE TESTING RESULTS
(Date Collected: 23 Jul 83; Time: 0750)

			Results of Analysis (ppm)			
Constituent Tested	Preserved/ Stabilized	Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	7 Aug	15			
Sulfite	Yes	7 Aug		5		
Causticity All	Yes	7 Aug			147.2	
(immediate test)	No	23 July	15	25	181.7	
(delayed test)	No	7 Aug	15	20	174.8	

TABLE 16

SAMPLE TESTING RESULTS
(Date Collected: 24 Jul 83; Time: 0755)

Constituent Tested	Preserved/ Stabilized		Results of Analysis (ppm)			
		Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	8 Aug	15			
Sulfite	Yes	8 Aug		15		
Causticity All	Yes	8 Aug			131.1	
(immediate test)	No	24 July	15	40	170.2	
(delayed test)	No	8 Aug	15	45	161	

TABLE 17

SAMPLE TESTING RESULTS
(Date Collected: 25 Jul 83; Time: 0755)

Constituent Tested			Results of Analysis (ppm)			
	Preserved/ Stabilized	Date Analyzed	Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	9 Aug	15			
Sulfite	Yes	9 Aug		35		
Causticity All	Yes	9 Aug			177.1	
(immediate test)	No	25 July	15	145	207	
(delayed test)	No	9 Aug	15	145	204.7	

TABLE 18

SAMPLE TESTING RESULTS
(Date Collected: 26 Jul 83; Time: 0750)

Constituent Tested	Preserved/ Stabilized	Date Analyzed	Results of Analysis (ppm)			
			Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	10 Aug	30			
Sulfite	Yes	10 Aug		70		
Causticity All	Yes	10 Aug			184	
(immediate test)	No	26 July	30	95	230	
(delayed test)	No	10 Aug	25	75	218.5	

TABLE 19

SAMPLE TESTING RESULTS
(Date Collected: 27 Jul 83; Time: 0740)

Constituent Tested		Date Analyzed	Results of Analysis (ppm)			
	Preserved/ Stabilized		Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	ll Aug	15			
Sulfite	Yes	ll Aug		15		
Causticity All	Yes	11 Aug	_		147.2	
(immediate test)	No	27 July	15	25	184	
(delayed test)	No	ll Aug	12	10	200.1	

TABLE 20

SAMPLE TESTING RESULTS
(Date Collected: 28 Jul 83; Time: 0744)

Constituent Tested	Preserved/ Stabilized	Date Analyzed	Results of Analysis (ppm)			
			Phos- phate	Sul- fite	Caus- ticity	
Phosphate	Yes	12 Aug	15			
Sulfite	Yes	12 Aug		75		
Causticity All	Yes	12 Aug			138	
(immediate test)	No	28 July	15	75	177.1	
(delayed test)	No	12 Aug	15	85	174.8	

APPENDIX E

CALCULATION OF DIFFERENCE PERCENTAGES

Phosphate Constituent (PPM)

Day of Experiment	Control Group (A)	Preserved/ Stabilized Group (B)	Unpreserv Group (C)	ved (A-B)	Percent Diff	(A-C)	Percent Diff
1	1	1	1	0	0	0	0
2	1	1	1	0	0	0	0
3	1	1	1	Ō	Ó	0	0
4	1	1	1	0	0	0	0
5	30 .	25	20	5	17	10	33
6	30	29	25	1	3	5	17
7	30	20	20	10	33	10	33
8	35	25	25	10	29	10	29
9	35	35	35	0	0	0	0
10	20	20	15	0	0	5	25
11	30	28	25	2	6	5	17
12	40	40	35	0	0	5	13
13	15	15	15	0	0	0	0
14	15	15	12	0	0	3	20
15	15	15	15	0	0	σ	0
16	15	15	15	0	0	0	0
17	15	15	15	0	0	0	0
18	30	30	25	0	. 0	5	17
19	15	15	12	0	0	3	20
20	15	15	15	0	0	0	0

Sulfite Constituent (PPM)

Day of Experiment	Control Group (A)	Preserved/ Stabilized Group (B)	Unpreser Group (C)	ved (A-B)	Percent Diff	(A-C)	Percent
1	45	5	40	40	89	5	11
2	60	10	55	50	83	5	8
2 3 4 5	35	5	25	30	86	10	28
4	20	5 5	10	15	75	10	50
5	65	5	50	60	92	15	23
6	105	20	75	85	81	30	29
7	30	10	25	20	67	5	5
8	70	10	45	60	86	25	36
9	75	15	65	60	80	10	13
10	230	20	150	210	91	80	35
11	205	15	85	190	93	120	59
12	45	15	30	30	67	15	33
13	25	15	15	10	40	10	40
14	85	15	60	70	82	25	29
15	25	5	20	20	80	5	20
16	40	15	45	25	63	- 5	-13
17	145	35	145	110	76	ó	0
18	95	70	75	25	26	20	21
19	25	15	10	10	40	15	60
20	75	75	85	0	0	-10	-13

Causticity Constituent (PPM)

Day of Experiment	Control Group (A)	Preserved/ Stabilized Group (B)	Unpreser Group (C)	ved (A-B)	Percent Diff	(A~C)	Percent Diff
1	90.6	87.4	94.3	3.2	4	-3.7	-4
1 2	126.5	117.3	126.5	9.2	7	0	0
3	117.3	103.5	110.4	13.8	12	6.9	6
3 4 5	115	94.3	110.4	20.7	18	4.6	4
5	218.5	196.8	211.6	21.7	10	6.9	3
6	299	282.9	299	16.1	5	0	0
7	200.1	142.6	197.8	57.5	29	2.3	3
8	154.1	115	158.7	39.1	25	-4.6	-3
9	167.9	112.7	165.6	55.2	33	2.3	1
10	78.2	69	87.4	9.2	12	-9.2	-12
11	119.6	66,7	87.4	52.9	44	32.2	27
12	177	119.6	172.5	57.4	32	4.5	3
13	267	239.2	269.1	27.8	10	-2.1	-1
14	142.6	119.6	147.2	23	16	-4.6	-3
15	181.7	147.2	174.8	34.5	19	6.9	4
16	170.2	131.1	161	39.1	23	9.2	5
17	207	177.1	204.7	29.9	14	2.3	1
18	230	184	218.5	46	20	11.5	5
19	184	147.2	200.1	36.8	20	-16.1	-9
20	177.1	138	174.8	39.1	22	2.3	1

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